A NEW TREATMENT OF FERRIC OXIDE HYDROSOLS

DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University

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W. F. FAIR, JR., A.B., M.A.

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PART I

1. Introductory

Among the contributions to the chemistry of so-called iron-oxy hydrosols, three originated in this laboratory. Thomas and Frieden,[1] studying iron oxychloride sols reported a constant ratio of iron to chloride when their sols were dialysed to incipient precipitation, and they offered the solution link theory to explain the nature of sol stability, according to which the micellar agglomerate was kept in solution by the solution forces inherent to the ferric chloride associated with the other constituents forming the micell. Hamburger[2] prepared iron oxybromide sols and reported no constant ratio of iron to anion (purity) although, on the whole, the bromide sols appeared to be more stable than the chloride sols studied simultaneously. Mabee[3] prepared and studied the properties of ferric oxyacetate hydrosols. He found a constant purity, and in general lower stability than was reported for the two types of sols previously studied. Both Hamburger and Mabee believed their results to be in harmony with an hydrolytic definition of hydrosols, and with the above mentioned solution link theory.

It was thought that a study of ferric oxypropionate sols might be an interesting comparison to these sols investigated earlier.

2. Preliminary Experiments

Ferric hydroxide was made by electrolysis (as described in Part II). Attempts to peptize this product with propionic acid seemed unsuccessful, and this method of sol preparation was discarded. It was thought that the precipitate was perhaps too granular and too little hydrated to be readily peptized. Next, some pure iron filings were dissolved in dilute propionic acid; after standing several days, during which there was a very slow evolution of hydrogen, a sample of the ferrous propionate solution was oxidized by treatment with hydrogen peroxide to absence of ferrous ion test with ferricyanide. (If the solution were not completely oxidized it was found that addition of ammonium

hydroxide yielded a black precipitate, which, upon drying, proved to be magnetic.)

The ferric propionate solution was then put into collodion membranes for dialysis to incipience of precipitation. In a very short time, small amounts of reddish-brown flocculate had appeared, so four different sols were immediately analysed, without centrifuging out the excess precipitated iron. The respective purities $\left(\frac{\text{equiv. Fe}}{\text{equiv. Anion}}\right)$ were found to be 1.2, 4.3, 3.8, and 1.1, while still another sample, intentionally dialysed somewhat beyond incipience of precipitation was found to have a purity of only 5.1.

In these analyses, the iron was determined[4] by heating to white fumes with sulfuric acid, passing through a Jones' reductor, and titrating with standardized permanganate solution. The propionate was determined[5] by heating, hydrolyzing, salting out, and titrating with standard sodium hydroxide solution, using phenophthalein as an indicator.

The fact that these iron propionate solutions should contain such a relatively small amount of iron in proportion to anion, as compared to sols previously studied, was entirely unexpected, and led to consideration of the possibilities suggested in the following section.

3. Theoretical

Besides the investigators already mentioned, several other colloid chemists have expressed beliefs that colloidal iron solutions underwent hydrolytic changes. Among these are Malfitano,[6] Buzágh,[7] Pauli and Matula,[8] Tian,[9] and others, but none of them has suggested any theoretical treatment or procedure to enlarge such beliefs. Therefore, the following development has been made, while fully realizing that in such complex systems as are dealt with, the considerations of equilibria must of necessity be rather loosely construed; this method of treatment is thus offered and utilized as a means to arrive at some interesting relations.

Keeping this in mind, we may say at once that if colloidal solutions are formed by progressive hydrolysis, they should follow laws analogous to those derived for the hydrolytic relationships from the law of mass action. According to these derivations, a salt of the type MA_3 may have two possibilities in hydrolysing, the distinction being based upon whether the acid formed is weakly or highly dissociated. First considering the strong acid type, from the equation $MA_3 + 3H_2O \rightleftarrows M(OH)_3 + 3HA$, letting x represent the amount hydrolyzed, and v the volume in

liters containing one mole of salt, and assuming both salt and acid to be completely ionized, we have

$$k = \frac{[M(OH)_3]\ [HA]^3}{[MA_3]\ [H_2O]^3}.$$

Since the (H_2O) is constant in aqueous solution,

$$K_{hyd.} = \frac{[M(OH)_3]\ [HA]^3}{[MA_3]} = \frac{\left[\frac{x}{v}\right]\left[\frac{3x}{v}\right]^3}{\frac{1-x}{v}} = \frac{27x^4}{(1-x)\ v^3}. \qquad (1)$$

Since $(H^+) \cdot (OH^-) = {}^sH_2O$,

then $[H^+] = 3x = \frac{{}^sH_2O}{[OH^-]}$,

so $[OH^-] = \sqrt[3]{K_{M(OH)_3} \frac{[M(OH)_3]}{[M^{+++}]}}$,

and since $[M^{+++}] = \frac{1-x}{v}$, then $[OH^-]^3 = K_{M(OH)_3} \frac{[M(OH)_3]}{\frac{1-x}{v}}$.

Moreover, $[\text{total acid}]^3 = \frac{{}^{s^3}H^2O}{K_{M(OH)_3} \frac{[M(OH)_3]}{\frac{1-x}{v}}}$

Therefore $K_{hyd.} = \dfrac{27x^4}{(1-x)\,v^3} =$

$$\frac{\left[\dfrac{s^3_{H_2O}}{K_{M(OH)_3}\dfrac{[M(OH)_3]}{\frac{1-x}{v}}}\right]}{\dfrac{[M(OH)_3]}{\frac{1-x}{v}}} = \frac{s^3_{H_2O}}{K_{M(OH)_3}}. \quad (2)$$

But when the acid formed by the hydrolysis is little ionized:

$$[M(OH)_3] = \frac{x}{v};\ [OH^-] = \sqrt[3]{K_{M(OH)_3}\frac{[M(OH)_3]}{[M^{+++}]}}.$$

$$[M^{+++}] = \frac{1-x}{v};\ \text{and}\ [A^-] = \frac{3(1-x)}{v}.$$

$$[OH^-] = \frac{s_{H_2O}}{[H^+]} = \frac{s_{H_2O}}{K_{HA}\dfrac{[HA]}{[A^-]}}.$$

$$K_{M(OH)_3}\frac{[M(OH)_3]}{[M^{+++}]} = \frac{s^3_{H_2O}[A^-]^3}{K^3_{HA}[HA]^3}.$$

$$K_{hyd.} = \frac{s^3}{K^3_{HA} \cdot K_{M(OH)_3}} H_2O = \frac{[M(OH)_3]\ [HA]^3}{[M^{+++}]\ [A^-]^3} =$$

$$\frac{\left(\frac{x}{v}\right)\left(\frac{3x}{v}\right)^3}{\left(\frac{1-x}{v}\right)\left(3\frac{1-x}{v}\right)^3} = \frac{x^4}{(1-x)^4}.$$

$$K_{hyd.} = \frac{x^4}{(1-x)^4} = \frac{s^3}{K^3_{HA} \cdot K_{M(OH)_3}} H_2O. \qquad (3)$$

Therefore in the latter type of hydrolysis the reaction is independent of dilution, whereas in the first type, the extent of the hydrolysis varies as $\sqrt[4]{v^3}$.

Now in the case of colloidal solutions, if we consider the complex as a somewhat soluble but little ionized *base*—into Fe^{+++} and OH^- ions—we have exactly the same conditions if the so-called chemical (hydrolytic) point of view of hydrosols is correct—up to the point of incipience of precipitation when the relations expressed above break down, and undergo a complete change due to the formation of insoluble bases. But from the point of true (ionic) solution through colloidal (micell) formation to the beginning of precipitation there is no apparent reason why colloidal iron solutions should not follow some such laws as those derived above, provided the solutions themselves are undergoing purely chemical reactions. This state of affairs might be expressed by some such system as

$$[Fe(OH)_3]_M \cdot (x)\ Fe^{+++} + 3\ (x)\ A^-$$
$$\downarrow\uparrow$$
$$(Fe^{+++}) + 3\ (OH^-)$$

This might be progressively hydrolyzed to

$$[Fe(OH)_3]_N \cdot (y)\ Fe^{+++} + 3\ (y)\ A^- + (x-y)\ HA$$
$$\downarrow\uparrow$$
$$Fe^{+++} + 3\ (OH^-)$$

where $x > y$, and $N > M$.

For a sol of purity = 20, the hydrolytic "equation" might be written as

$$20\ Fe\ A_3 + 57\ H_2O \rightleftarrows [Fe\ (OH)_3]_{19} \cdot Fe\ A_3 + 57\ HA$$

As the acid formed is dialysed away, the sol would analyse to 60 equiv. Fe and 3 equiv. anion, thereby giving a purity of 20. If dialysis were continued, successive stages of hydrolysis would be reached, more $Fe\ (OH)_3$, less (Fe^{+++}) and (A^-) present, and hence higher purities. Then for the progressive hydrolysis of iron salts to colloidal solutions we have the two types of reactions, and the respective "colloidal hydrolysis constants":

$$K_{c.hyd.} = \frac{s^3 H_2O}{K_b} = \frac{27_x{}^4}{(1-x)v^3} \qquad (4)$$

and

$$K_{c.hyd.} = \frac{s^3 H_2O}{K^3{}_a \cdot K_b} = \frac{x^4}{(1-x)^4} \qquad (5)$$

where K_a is the dissociation constant of the acid formed, and K_b represents the dissociation constant of the complex colloidal radical *as a base*.

Then the colloidal solutions of ferric chloride, bromide, nitrate, etc., should follow (4) while those of the acetate, propionate and butyrate should follow (5).

Now although we do not know the respective K_b values of various iron colloids, at least we may safely assume that they are very small, and of the same order of magnitude.

Then if we consider the two salts $Fe\ (A_1)_3$ and $Fe\ (A_2)_3$, both of which form weak acids upon hydrolysis, we may write as the relation between their respective "colloidal hydrolysis constants":

$$\frac{K_1}{K_2} = \frac{\dfrac{s^3 H_2O}{K^3{}_{HA_1} \cdot K_{b_1}}}{\dfrac{s^3 H_2O}{K^3{}_{HA_2} \cdot K_{b_2}}} = \frac{K^3{}_{HA_2}}{K^3{}_{HA_1}} \qquad (6)$$

Then we see that the ratio of the "constants" is inversely proportional to the cubes of the dissociation constants of the respective acids produced by the hydrolysis, after having assumed that K_{b1} and K_{b2} are nearly equal.
If we call R, this ratio—

$$\frac{K_1}{K_2} = \frac{K^3_{HA_2}}{K^3_{HA_1}} = R \quad \text{then it is also true that}$$

$$R = \frac{\dfrac{x_2{}^4}{(1-x_2)^4}}{\dfrac{x_1{}^4}{(1-x_1)^4}} \quad \text{from which} \tag{7}$$

$$\frac{x_2}{1-x_2} = \sqrt[4]{R} \cdot \frac{x_1}{1-x_1} \tag{7a}$$

or in other words the fraction hydrolyzed of one salt will always be a constant times the fraction hydrolyzed of the other salt (under the same conditions of time and temperature).

Dividing both sides of equation (7) by $x_1{}^4$, and multiplying both sides by $x_2{}^4$, we arrive at

$$\frac{\left(\dfrac{1}{1-x_1}\right)^4}{\left(\dfrac{1}{1-x_2}\right)^4} = \frac{x_2{}^4}{x_1{}^4} \cdot R$$

therefore

$$\frac{\dfrac{1}{1-x_1}}{\dfrac{1}{1-x_2}} = \frac{x_2}{x_1} \sqrt[4]{R}$$

Now as soon as appreciable purities are reached—high ratios of iron over anion—x_1 and x_2 become very nearly equal; and $\frac{1}{1-x}$ is equal to the purity at incipience of precipitation as previously defined, therefore approximately,

$$\frac{P_1}{P_2} = \sqrt[4]{R} \tag{8}$$

But for weak acids, R is quite small—for acetic and propionic it is only 2.4—so we may conclude that very nearly equal purities at incipience of precipitation should be found for two iron salts, both of which yield weak acids upon hydrolyzing.

Another interesting application when a weak acid is formed is seen in the equalities set down below:

$$(H^+) = K_{HA}\frac{(HA)}{(A^-)} = K_a\frac{x}{1-x} = K_a\sqrt{\frac{s^3}{\frac{H_2O}{K_a^3 \cdot K_b}}} \tag{9}$$

or, (H^+) = a constant (10)

Also, it is interesting to point out that from equation (9) one may find the magnitude of K_b, if the pH is first determined.

Such calculations cannot be applied to sols where a strong acid is formed, first because the changing dilution during dialysis must change the purity relationships and, secondly, because the acid is dialysed away, and there is no constancy possibly here as was the case with the acetate.

Now again turning to the strong acids, it is evident, since the extent of the hydrolysis varies as $\sqrt[4]{v^3}$, that constant optimum purity values can be obtained only if no dilution takes place during dialysis. In other words, the purities of this type of sol, at incipient precipitation should *not* be constant. Neidle[10] reports this qualitatively for the oxychloride, Hamburger[2] for the ferric oxybromide sol. Thomas and Frieden[1] report a constant purity for ferric oxychloride sol, but this may be due to the fact that the determinations were made on a sol of low concentration, which was divided into samples of various dilutions, after first undergoing the same preliminary dialysis, both of which procedures would help in masking differences in the sols at the end of the experiments.

In comparison with these results, the work of Sorum,[12] who reports chloride-free iron hydrosols, and Bradfield,[13] who made

high purity sols by a centrifuge method, are interesting; Weiser's discussion of sol purity as given in his well-known "Hydrous Oxides" (pp. 47-48) is also of interest in this matter.

It has been known for a long time that $SO_4^{=}$ ion was a good precipitation or flocculation agent for iron oxysols.

The theoretical derivations demand this, as may be seen from the following relationships:

$$Fe_2(SO_4)_3 + 6\ H_2O \rightleftarrows 2\ Fe\ (OH)_3 + 3\ H_2SO_4.$$

Using the same notations,

$$K = \frac{[Fe(OH)_3]^2\,[H_2SO_4]^3}{[Fe_2(SO_4)_3]} = \frac{\left(\frac{2x}{v}\right)^2\left(\frac{3x}{v}\right)^3}{\frac{1-x}{v}} = \frac{108x^5}{(1-x)v^4}.$$

$$\text{Also } [H^+] = \frac{{}^{s}H_2O}{[OH^-]},\ [\text{total acid}] = \frac{1}{2}[H^+],\ \text{and } [OH^-] = \sqrt[3]{K_{Fe(OH)_3}\frac{[Fe(OH)_3]}{[Fe^{+++}]}}.$$

$$\text{Then } [\text{total acid}]^3 = \tfrac{1}{8}\left(\frac{{}^{s^3}H_2O}{[OH^-]^3}\right) = \tfrac{1}{8}\,\frac{{}^{s^3}H_2O}{K_{Fe(OH)_3}\frac{[Fe(OH)_3]}{[Fe^{+++}]}}$$

$$K = [Fe(OH)_3]^2 \cdot \tfrac{1}{8} \frac{s^3_{H_2O}}{K_{Fe(OH)_3} \frac{[Fe(OH)_3]}{[Fe^{+++}]}} \div [Fe_2(SO_4)_3]$$

$$= \frac{\left(\frac{2x}{v}\right)^2 \cdot \frac{s^3_{H_2O} \cdot 2\left(\frac{1-x}{v}\right)}{8 K_{Fe(OH)_3} \cdot 2\left(\frac{x}{v}\right)}}{\frac{1-x}{v}}$$

$$= \frac{s^3_{H_2O} \cdot x}{2 K_{Fe(OH)_3} \cdot v} = \frac{108x^5}{(1-x)v^4}. \quad (11)$$

from which it is evident, comparing equation (11) with equation (4), that K for ferric sulfate must be smaller than in the case of the chlorides, bromides, etc., for x is always less than 1, (in the case of the sulfate, indeed, it is probably very small) and V is always greater than one, as fairly dilute solutions must be used if colloidal solutions are to be formed. In addition we have the factor 2 appearing in the denominator which would make the sulfate even less "colloidal" compared to the other strong acid types.

The micell as pictured according to the above relationships agrees very closely with the "solution link" theory of colloidal stability, the ferric hydroxide formed by the hydrolysis being dragged into solution by a soluble ferric salt which has previously been called the peptizing agent. As hydrolysis proceeds, the $Fe(OH)_3$ chain gets larger and larger until finally there is not enough of the peptizing agent present, and precipitation occurs. It should be noted that the law of mass action as used above, has always been applied to the ("solution link") salt—not to the dispersed phase.

If the views here presented are the correct explanation of iron hydro-sol stability, it would be natural to expect that flocculation should occur in a manner similar to ordinary precipitation

due to the formation of insoluble compounds. Opponents of the chemical theory of hydrosol behavior have long used the known facts of different amounts of anions (sulfates, for instance), for sol precipitation in apparently no chemical or equivalent relationships, in their arguments. Nevertheless, it is possible that flocculation may be due to the formation of insoluble compounds which precipitate when a certain relationship similar to a solubility product constant is exceeded, and a theory is presented below in an endeavor to reconcile the conflicting views and evidence in this interesting matter.

As was pointed out above, the iron salt upon hydrolyzing acquires a longer and longer $Fe(OH)_3$ tail, or chain, the sol becoming more unstable as the purity rises. Then coinciding with this progressive hydrolysis it is not too far-fetched to expect successively lower "solubility product constants" (called below ion product constant) with successive hydrolytic stages (*i.e.*, as N in $[Fe(OH_3)]_N \cdot FeA_3$ increases). According to this hypothesis the amount of sulfate necessary for precipitation should *decrease* with rising purity, which corresponds to lower Fe^{+++} ion concentration, as opposed to the analogous inorganic (ionic) solutions where a higher anion concentration is required, if the cation concentration is lowered, to satisfy a $K_{s.p.}$ As pointed out above, the reason for this anomaly is that as the purity increases the Fe^{+++} concentration decreases, but as the constant governing the precipitation is also becoming successively smaller to govern the new conditions of the next stage of hydrolysis then the SO_4 = concentration necessary for precipitation also decreases.

However, if there be any such governing factor analogous to a $K_{s.p.}$ it is evident that the ratio of Fe^{+++} ions to SO_4 = ions in moles per liter should remain constant throughout the range of purity changes. Below are calculations from the data of Hamburger's dissertation, page 20:

TABLE V.—(Fe/Liter = 415 Milli. equiv.)

Fe/Cl or P	(Fe^{+++}) in m.m./l.	$(SO_4 =)$ m.m./l.	Ratio $\left(\frac{SO_4 =}{Fe^{+++}}\right)$
20	7	5.05	.72
23	6	3.94	.65
24	5.7	3.94	.69
25.7	5.4	3.49	.65
30.3	4.6	2.69	.58
		Average	.66

In the above table Fe/Cl, or purity, and $SO_4 =$ (in milli-mols) are reported. (Fe^{+++}) in milli-mols per liter has been calculated from

$$\frac{\text{Total Fe (in milli-equiv.)}}{P} = \text{anion}$$

and $$\frac{\text{anion}}{3} = Fe^{+++} \text{ (in milli-mols).}$$

Thus the ratio $\frac{SO_4 =}{Fe^{+++}}$ was computed. Similar calculations are given in the tables that follow. (The error in measuring the precipitation or "liminal" values, defined as the average between the amount just flocculating, and that failing to precipitate, is about $\pm$ 5%.)

The above table showed the precipitation values for a chloride sol; below are the values for a bromide sol.

TABLE IV.—(Fe/Liter = 415 m. equiv.)

Fe/Br	(Fe^{+++}) in m.m./l.	($SO_4 =$)	Ratio $\left(\frac{SO_4 =}{Fe^{+++}}\right)$
20.4	6.7	7.47	1.11
22.2	6.2	7.15	1.15
25.6	5.4	6.12	1.13
25.7	5.37	5.96	1.10
29.8	4.6	5.00	1.09
33.5	4.1	4.24	1.03
38.5	3.6	3.65	1.01
41.8	3.3	3.62	1.10
			Average 1.09

Thus we see that these ratios are in harmony with the known facts concerning the relative stabilities of the two halides as "solution links." In other words, ferric oxy (bromide) sulfate is more soluble than ferric oxy (chloride) sulfate, at the same purity.

From Mabee's dissertation (pp. 31, 34 and 35) we can use data for the ferric acetate sols he studied, and make similar calculations:

Fe/l.	Fe/Ac	Fe^{+++} in m.m./l.	$SO_4 =$	Ratio $\left(\frac{SO_4 =}{Fe^{+++}}\right)$
567	12	15.7	1.7	.108
358	12.8	9.3	.95	.102
555	13	14.2	2.0	.14
567	20*	9.4	1.0†	.106
358	20*	5.9	.5†	.084
555	20*	9.3	1.0†	.107
			Average	.108

*The value given by Mabee for purity at incipient precipitation.
†Values read off aging data at description of "brown, turbid," indicating incipient precipitation.

Thus, ferric oxy (acetic) sulfate is less soluble than the other two considered above, which is in complete harmony with the known facts about these sols.

Using the above average values for the respective ratios, $\left(\frac{SO_4 =}{Fe^{+++}}\right)$, we can readily calculate from Hamburger's $SO_4 =$ values, initially, and at precipitation (for this the values were taken from the dotted line indicating incipience of precipitation in the tables) the purity of the sols at these two stages of aging. (The data used below are taken from Tables VII to XII, pp. 24-26); from the average ratio value as found above, and the reported ($SO_4 =$) value, Fe^{+++} can be calculated. The total Fe in milli-equiv. divided by this (Fe^{+++}) gives the purity.

Sol	Table	Total Fe/ m. equiv./l.	Init. $SO_4 =$ m.m./l.	Initial Calc. Fe^{+++}	Initial Calc. P	Initial Analyt P	Pptation $SO_4 =$	Calc. Fe^{+++}	Pptation (calc.) P
Br	VII	415	7.74	21	19.8	20.4	6.68	18.3	22.6
Cl	VIII	415	5.05	23	18.0	20.0	4.66	21.0	19.8
Br	IX	415	5.96	16.2	25.6	25.5	(6.20)*	16.8	24.5
Cl	X	412	3.50	15.9	25.9	25.7	(3.40)*	15.3	26.9
Br	XI	415	4.24	11.6	35.7	33.5	4.67	12.7	32.7
Br	XII	402	3.26	9.0	44.7	40.3	(3.67)*	10.0	40.3

*Interpolated at dotted line.

In some instances above, the precipitation purity is less than the starting purity. This discrepancy may be due to the fact that the difference between the initial and precipitation $SO_4 =$ values

is less than the 5% error in determining these values. Similarly the allowable difference between calculated P and analytically determined P at the start is also at least ± 5%.

Since the calculated initial P agrees fairly well with P by analysis, it seems that this calculation should apply equally well to P at incipient precipitation, and thus it will be noted in the above table that the purity upon aging to incipient precipitation is *not* constant for either bromide or chloride sols which is in accordance with the predictions based upon hydrolytic considerations given in the derivations above. The reason for these P's being so low compared to previously reported values is that these solutions are much more concentrated than those dialysed to precipitation.

Returning now to the idea of a "$K_{s.p.}$", if we consider the micell as $[Fe(OH)_3]_N \cdot Fe\ A_3$ to present an exceedingly simplified picture, then for a "solubility product" at any particular hydrolytic stage, we could write (for the sulfate)—

"$K_{s.p.}$" $= ([Fe(OH)_3]_N \cdot Fe^{+++})^2\ (SO_4 =)^3$, or merely,

$(Fe^{+++})^2\ (SO_4 =)^3$, (Fe^{+++}) being calculated from $\left(\frac{\text{total Fe}}{P}\right)$; but it was thought best in developing the analogy to refrain from calling this constant a "$K_{s.p.}$" since it cannot definitely be stated what solid phase is in equilibrium with the constant. It was therefore decided to name this constant an "ion product constant":

$(Fe^{+++})^2\ (SO_4 =)^3 = K_{i.p.}$, a factor governing the conditions existing in a sol at the determintion of its sulfate liminal value.

For the different stages in the acetate sols tabled above, this would give:

(1) $K_{i.p.} = (15.7 \times 10^{-3})^2\ (1.7 \times 10^{-3})^3 = 1.2 \times 10^{-12}$.
(2) $K_{i.p.} = (9.3 \times 10^{-3})^2\ (.95 \times 10^{-3})^3 = 7.4 \times 10^{-14}$.
(3) $K_{i.p.} = (14.2 \times 10^{-3})^2\ (2 \times 10^{-3})^3 = 1.6 \times 10^{-12}$.
(4) $K_{i.p.} =$ Same as (6).
(5) $K_{i.p.} = (6 \times 10^{-3})^2\ (.5 \times 10^{-3})^3 = 4.5 \times 10^{-15}$.
(6) $K_{i.p.} = (9.3 \times 10^{-3})^2\ (1 \times 10^{-3}) = 8.6 \times 10^{-14}$.

It appears by inspection that the respective successive $K_{i.p.}$'s progress exponentially, with increase in P. If there is such an exponential progression, then if P is the purity, the $P^{\frac{1}{n}}$ root of the $K_{i.p.}$ at that purity should give the $K_{i.p.}$ of ferric oxy (halide) sulfate when x is exceedingly small. From which it is imme-

diately apparent that if we take the root (of different $K_{1.p.,s}$) corresponding to the purities, we should obtain the same value. (It should be noted here that taking large roots of numbers less than 1, tends to give a value approaching 1.)

Below is a table showing these values, found by taking the P^{th} root of the $K_{1.p.,s}$ as calculated above:

(1)	.1015	1 to 2×10^{-1} for acetate.
(2)	.095	
(3)	.0102	
(4)	.222	
(5)	.191	
(6)	.222	

For the chloride (from Table V):

	$K_{1.p.}$	$\sqrt[P]{K_{1.p.}}$	
(1)	6×10^{-12}	.27	3 to 4×10^{-1}.
(2)	2×10^{-12}	.31	
(3)	1.8×10^{-12}	.32	
(4)	1.2×10^{-12}	.35	
(5)	4×10^{-13}	.39	

For the bromide sols (Table IV):

	$K_{1.p.}$	$\sqrt[P]{K_{1.p.}}$	
(1)	1.8×10^{-11}	.29	3 to 5×10^{-1}.
(2)	4.4×10^{-12}	.33	
(3)	6.6×10^{-12}	.37	
(4)	2.6×10^{-12}	.41	
(5)	1.2×10^{-11}	.47	
(6)	6.6×10^{-13}	.48	
(7)	5×10^{-13}	.5	

Thus we see that all give a value of the same order of magnitude — 10^{-1}, which is remarkable under the conditions, and certainly cannot be due to chance, but is very good support for this general theory. Of course, the above calculations may be reversed, and we may predict the amount of $SO_4 =$ necessary to precipitate a given iron sol:

$$(SO_4 =) = \sqrt[3]{\frac{(k)^P}{\left(\frac{Fe}{P}\right)^2}}, \text{ where k is about } 10^{-1},$$

P is the purity and (Fe) the total iron.

Every bit of evidence presented above is strictly in accordance with the chemical-hydrolytic definition of iron hydrosols, based upon the law of mass action. The theory of preferential ionic adsorption seems unnecessary to explain iron sol behavior, and if there is such a phenomenon as preferential ionic adsorption in these systems, the effects of such adsorption seem to be governed by the law of mass action, as applied to the solution link part of the micell.

4. Experimental

In accordance with the hypothesis presented above, the following generalities should be considered:

(1) The purity of a sol, at incipient precipitation, of the chloride type, should increase with dilution.

(2) At incipient precipitation, sols of the weak acid type should have constant purities, independent of dilution.

(3) For two sols of the weak acid type, the difference in their respective purities at incipient precipitation should depend upon the relative values of the dissociation constants of the acids formed; therefore their purities should be nearly equal.

(4) From the liminal value—ion product constant relation, it is evident, if the ideas presented above are correct, that peptization should occur even if sulfate be present, and the greater the concentration of sulfate, the smaller the final obtainable purity, provided the chloride (or other anion) remain constant.

For the purpose of testing these ideas, the following peptization experiments were started:

Sol No.	$Fe(OH)_3$ Suspension	Acid	Nacid	C.c. Acid	C.c. H_2O	C.c. (M/2) (Na_2SO_4)
1	40 c.c.	Acetic	.0853	200	10	
2	" "	"	"	150	60	
3	" "	"	"	100	110	
4	" "	Butyric	.0871	200	10	
5	" "	"	"	150	60	
7	" "	Propionic	.0884	200	10	
8	" "	"	"	150	60	
9	" "	"	"	100	110	
11	100 "	HCl	.50	15	135	
12	" "	"	"	25	125	
13	40 "	Propionic	.0884	200	0	
15	" "	"	"	200	0	
16	" "	Butyric	.0871	200	0	
17	" "	"	.0871	200	0	
18	" "	"	"	200	0	
19	" "	Acetic	.0853	200	0	
21	" "	"	"	200	0	
22	20 "	Propionic	.0884	200	0	
23	" "	"	"	200	0	
24	" "	Butyric	.0871	200	0	
25	" "	"	"	200	0	
26	" "	Acetic	.0853	200	0	
27	" "	"	"	200	0	
28	100 "	HCl	.520	19.2	280.8	
33	" "	"	"	11.5	288.5	0
34	" "	"	"	11.5	287.5	1
35	" "	HCl	.520	11.5	286.5	2
36	" "	"	"	"	285.5	3
37	" "	"	"	"	283.5	5

The ferric hydroxide used in the above series was prepared by slow precipitation from the chloride with ammonium hydroxide and then washing daily by decantation with large volumes of water (about 25 liters) for six weeks, until samples of the wash water gave no test whatsoever with equal volumes of · IN silver nitrate solution on six successive days. The acids used were the purest obtainable from the Eastman Kodak Co., and were standardized against known sodium hydroxide solution. In all cases there was excess of ferric hydroxide. After standing nine months these solutions were analyzed, after being centrifuged for sixty minutes at about 1000 r.p.m. The iron and organic anions were determined as in the preliminary part described above; the chloride in a similar manner; and the sulfate as the barium salt. The results are given in the following tables:

TABLE 1.—(Acetate)

Sol	Iron (M. eq./l.)	Anion (M. eq./l.)	Purity
1	114	68.2	1.7
2	141	51.2	2.8
3	135	34.1	4.0
19	148.5	71.1	2.1
20	123	66.1	1.9
21	127.5	71.1	1.8
26	130.5	71.1	1.8

TABLE 2.—(Butyrate)

Sol	Iron (M. eq./l.)	Anion (M. eq./l.)	Purity
4	57	70	0.8
5	66	52.3	1.7
16	82.5	72.6	1.1
17	88.5	72.6	1.2
18	76.5	72.6	1.1
24	52.5	22.6	2.3
25	45.0	23.6	1.9

TABLE 3.—(Propionate)

Sol	Iron (M. eq./l.)	Anion (M. eq./l.)	Purity
7	147	70.7	2.0
8	138	53.0	2.6
9	153	35.4	4.3
13	147	73.6	2.0
15	158	73.6	2.1
22	100.5	73.6	1.3
23	142.5	73.6	1.9

TABLE 4.—(Chloride)

Sol	Iron (M. eq./l.)	Anion (M. eq./l.)	Purity
11	324	30	10.8
12	338	50	6.8
28	346.5	25	13.9
33	366	12.5	29.3

TABLE 5.—(Chloride and SO_4 =)

Sol	Iron (M. eq./l.)	Cl (M. eq./l.)	SO_4 (M.M./l.)	Purity $\left(\frac{Fe}{Cl}\right)$
33	366	12.5	0	29.3
34	339	12.5	1.3	27.1
35	336	12.5	2.5	26.9
36	126	12.5	3.8	10.8
37	(No apparent peptization—clear solution)			

In Table 6 are shown the results obtained with the same three weak acids but with ferric hydroxide that had been washed only a few times, and so still contained occluded chloride. Anion calculated from Nacid—and final volume.

TABLE 6

Sol	Iron (M. eq./l.)	Anion (M. eq./l.)	Purity
Chloride	241	17	14.2*
Acetate	195	21.7	9.0
Propionate	186	22.1	8.4
Butyrate	180	21.8	8.2

*(No Fe_2O_3 residue, all added was peptized.)

The results of this last experiment indicated that Mabee's value of 20 (as against the low purity shown in Table I) might be due to the presence of chloride in his sols. Fortunately, there was available in the laboratory some of the iron acetate he used as well as one of his sols. Both gave white precipitates upon addition of silver nitrate, after heating with nitric acid.

An iron propionate solution from iron filings and pure acid, oxidized with hydrogen peroxide and centrifuged, gave a purity of 1.1 upon analysis. Similarly, using acetic acid, a purity of slightly less than one was obtained.

It is at once apparent that these results are in accordance with the main points outlined above, and hence help to strengthen the hydrolytic point of view of micell stability, and the chemical reaction ("solubility product" or ion product) idea of sol precipitation. It also seems quite probable that Mabee really studied a mixture of ferric oxychloride sol and ferric acetate sol, and thus found properties intermediate between the two. The differences between two sols of the weak acid type apparently are too small to be significant in view of the fact that this type of sol in general appears to peptize such extremely small amounts of $Fe(OH)_3$.

PART II

1. Introductory

According to Reinders,[11] and Hoffman,[11] who noted the wetting effect of certain solvents on powders of different degrees of fineness, organic solvents, when shaken with an iron sol, should not affect the sol, since they do not wet the dispersed particles. According to the solution link theory, the organic liquid should affect the sol if the stabilizing salt (solution link) is affected by the solvent; if the solvent is miscible with water, and the salt providing the solution stability is insoluble in the organic solvent, the sol should precipitate; on the other hand, if the solvent is immiscible with water but the peptizer is soluble, the dispersed particles should be attracted toward the organic liquid. If the solvents are miscible and the salt soluble in the organic liquid, no precipitation or partition should occur.

As a means of examining qualitatively these opposing theories, it was decided to put pure Fe_2O_3 into systems composed of water, an organic solution immiscible with water, and a peptizing agent more soluble in one liquid than in the other. Observation of the layer to which the Fe_2O_3 particles tended to be attracted would then indicate whether the particles were being dispersed by the influence of ions and electric charges (absorption theory) or by solution forces (solution link theory).

2. Experimental

Peptization of $Fe_2(O)_3$ in Two Layer Systems

The $Fe_2(O)_3$ used was prepared by electrolysis of tap water, using a pure iron anode and a carbon cathode. To furnish sufficient conductivity, 10 c.c. of approximately 6N Na OH was added to the water in the electrolyzing tank which had a volume of about 30 liters; the concentrations of Na^+ and OH^- ions were therefore not more than about $\frac{N}{500}$. A current of air was bubbled through continuously to oxidize the $Fe(OH)_2$ first formed, and the resulting $Fe(OH)_3$ was then washed to free it as far as possible from the few ions that might still be present.

In setting up series Y and W the moist $Fe(OH)_3$ was introduced as prepared above; in series X and Z, the precipitate was first washed with alcohol, then with ether, and finally wet with the organic solvent with which it was later to be mixed, as indicated in the tables below. Series Z and W were merely con-

trols, showing the behavior of $Fe(OH)_3$ in water—organic solvent systems without the peptizing acid.

The respective mixtures were made by adding to 100 c.c. of water, 100 c.c. of the organic solvent, then some of the $Fe(OH)_3$ and the acid. These mixtures were shaken occasionally and allowed to stand over a period of about six months. The systems set up and the results observed are given below:

o.	Org. Liquid	Pep. Acid	Pep. Acid more Soluble in	Observations: $Fe(OH)_3$ in
-1	Anyl alcohol	Acetic	Water	Lower aqueous layer
-1	" "	"	"	" " "
-2	Chloroform	"	"	Upper " "
-2	"	"	"	" " "
-3	Ether	Benzoic	Ether	" ether "
-3	"	"	"	" " "
-4	Chloroform	"	Chloroform	" layer; lower dark colored
-4	"	"	"	" " coarse precipitate; lower turbid
-5	Benzene	"	Benzene	" benzene layer
-5	"	"	"	" " "
-6	Anyl alcohol	"	Anyl alcohol	" alcohol layer
-6	" "	"	" "	" " "
-7	Toluene	"	Toluene	" toluene layer
-7	"	"	"	" layer turbid, coarse precipitate emulsion floating at top of lower liquid
-8	Carbon tetrachloride	"	Cinnamic	Lower CCl_4 layer; some at interface
-8	"	"	"	Same as Y-4 in appearance
-9	Ether	Citric	Water	Bottom; lower aqueous layer yellow
-9	"	"	"	" " " " "
-10	"	Fumaric	Equal solubility	" " " " "
-10	"	"	" "	" " " " "
-11	"	Malic	Water	" " " " "
-11	"	"	"	" " " " "
-12	"	Salicylic	Ether	Upper ether layer; lower red
-12	"	"	"	" " " " "
-13	Benzene	"	Benzene	A solid clump hanging from interface
-13	"	"	"	Lower aqueous layer and interface
-14	Chloroform	"	Chloroform	Upper aqueous layer; lower colored
-14	"	"	"	" " " " "
-15	Carbon tetrachloride	"	Water	" " "
-15	"	"	"	" " "

Checks:	Org. Liquid	Observations: $Fe(OH)_3$ in
W-1	Anyl Alcohol	(On) bottom
Z-1	" "	" "
W-2	Chloroform	Upper aqueous phase
Z-2	"	" " "
W-3	Ether	Lower aqueous phase
Z-3	"	" " "
W-4	Benzene	Interface, emulsified
Z-4	"	" "
W-5	Toluene	Lower aqueous layer
Z-5	"	Interface, emulsified; same on bottom
W-6	Carbon tetrachloride	Upper aqueous layer
Z-6	"	" " "

From the foregoing it seems that in the system studied, Fe_2O_3 tends to go to the aqueous phase if no peptizing acid is present, but if a peptizer is present, then $Fe(OH)_3$ tends in general to disperse in the phase in which the acid is the more soluble, even if that phase constitutes the upper layer of the system, which makes it all the more difficult to drag up the heavy Fe_2O_3.

SUMMARY

1. The purities at incipient precipitation of iron hydrosols are in agreement with the hydrolytic definition of sols.

2. A chemical theory of sol precipitation, based upon the solubility product concept is supported by the experimental data.

3. Weak acids, acetic, propionic and butyric, bring little more than equivalent amounts of iron into solution, but small amounts of chloride will greatly increase the amount of iron peptized.

4. In systems composed of iron hydroxide, water, organic water-immiscible solvent, and peptizing acid, the iron hydroxide is attracted toward that layer in which the acid is the more soluble.

5. All the above is in agreement with the Chemical-Complex theory of hydrosols.

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